THE STRUCTURE OF MALABARICOL

William F. Paton and Iain C. Paul
Department of Chemistry, University of Illinois
Urbana, Illinois, 61801, USA

and

Ashok G. Bajaj and Sukh Dev
Malti-Chem Research Centre, Nandesari, Vadodara, India

Abstract: A single crystal X-ray analysis has confirmed the constitution and established the stereochemistry of the triterpene, malabaricol.

Malabaricol, the chief triterpene constituent of the oleoresin of Ailanthus malabarica DC, was assigned the unique and biogenetically fascinating structure I, on the basis of spectral data biogenetic reasoning, and key chemical degradations.[1,2] A direct chemical correlation[2] with (+)-ambreinolide (II) led to the definition of its absolute stereochemistry at all chiral centers ex-

I

II

III
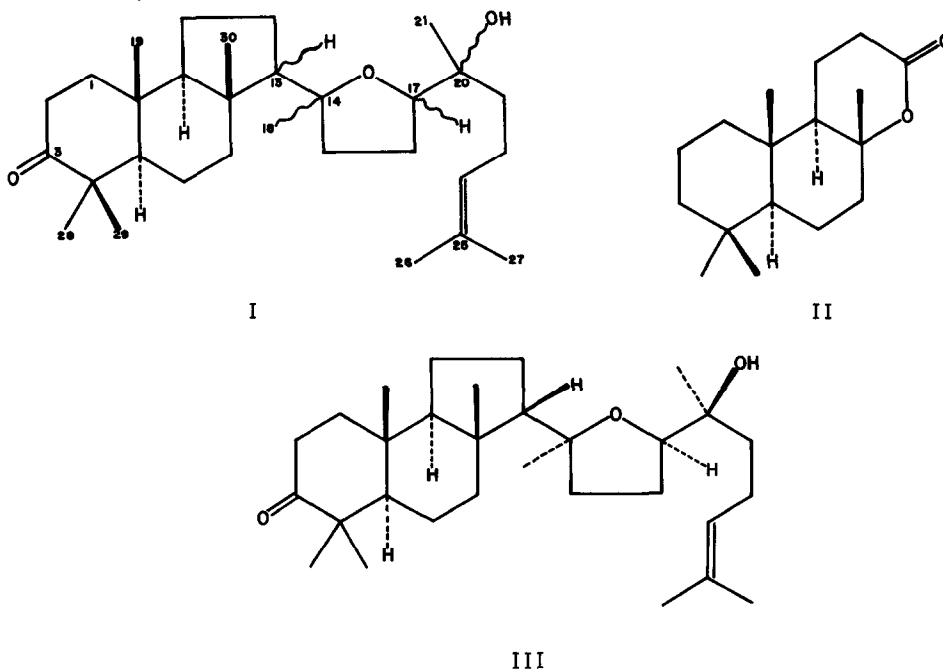
cept C_{13}, C_{14}, C_{17}, and C_{20}. Sharpless[3] was able to synthesize the closely-related d,ℓ-malabari-canediol from a squalene derivative and showed that the stereochemistry at C_{17} and C_{20} (our numbering) was that arising from a formal trans hydroxylation of that double bond in squalene. Based on a biogenetic hypothesis developed in his thesis,[4a] he also proposed configurations at C_{13} and C_{14}.[4b] In view of the considerable biogenetic importance of the structure and stereochemistry of malabaricol, it was considered desirable to carry out a single crystal X-ray analysis.
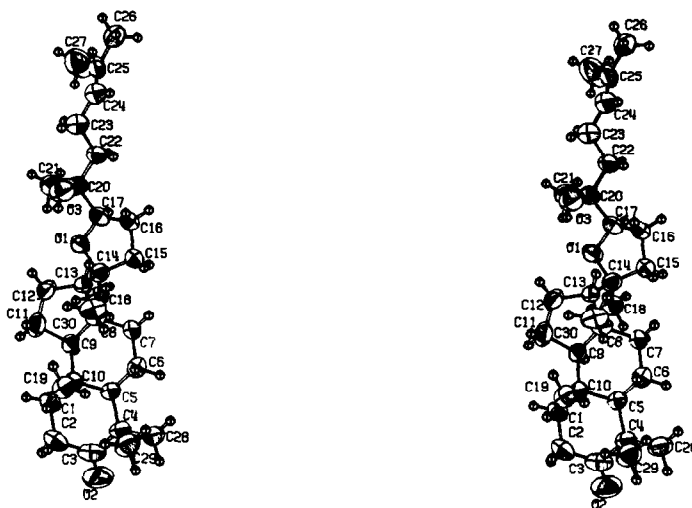
Figure I: A stereoscopic view of the structure of malabaricol.

Crystals of I suitable for X-ray work were obtained from acetonitrile. Crystal Data: $C_{30}H_{50}O_3$, M.W. = 458.7, orthorhombic, $\underline{a}$ = 6.670(1), $\underline{b}$ = 11.463(2), $\underline{c}$ = 36.644(6)$\overset{\circ}{A}$, $\underline{V}$ = 2801.7$\overset{\circ}{A}^3$, $\underline{Z}$ = 4, ρ_{calc} = 1.09 g cm^{-3}, $\underline{\mu}$(MoK$_\alpha$) = 0.7 cm^{-1}, space group $\underline{P2_12_12_1}$. Intensity data were collected on a Syntex $\underline{P2_1}$ diffractometer at ambient room temperature with a total of 1458 non-zero reflections being obtained at the 2σ-level of significance (out of 2868 possible independent reflections). The structure was solved by the use of MULTAN.[5] The structure was refined by full-matrix least squares methods to a final $\underline{R}$-factor of 0.074 and a weighted $\underline{R}$-factor of 0.054 on all non-zero reflections. Further details of the X-ray work will be reported elsewhere.[6]

A stereoscopic view of the molecular structure is shown in Figure I and the stereochemistry is as shown in (III). The constitution and stereochemical determinations established previously[1,2] are confirmed. The configurations at C_{13}, C_{14}, C_{17} and C_{20} are shown to be $\underline{S},\underline{S},\underline{R}$, and $\underline{S}$, respectively.

References and Notes:

1. A. Chawla and Sukh Dev, Tetrahedron Letters, 4837 (1967).

2. R. R. Sobti and Sukh Dev, Tetrahedron Letters, 2215 (1968).

3. K. B. Sharpless, J. Am. Chem. Soc., 92, 6999 (1970).

4. (a) K. B. Sharpless, Ph.D. Thesis, Stanford University, 1968; (b) One aspect of his hypothesis relates to the mode of folding of the polyene chain during cyclization. It is noted that all known cyclic triterpenes arise from chain folding of incipient ring C. Sharpless has informed us that in his original publication[3] he inadvertently drew the R configuration at C_{14} when the S configuration, demanded by chain folding of incipient ring C, was intended.

5. G. Germain, P. Main, and M. M. Woolfson, Acta Cryst., A27, 368 (1971)

6. W. F. Paton and I. C. Paul, Cryst. Str. Comm., in press (1979).